1-1-2015

Nutrient and trace organic contaminant removal from wastewater of a resort town: comparison between a pilot and a full scale membrane bioreactor

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Disciplines

Engineering | Science and Technology Studies

Publication Details

Phan, H. V., Hai, F. I., McDonald, J. A., Khan, S. J., Zhang, R., Price, W. E., Broeckmann, A. & Nghiem, L. D. (2015). Nutrient and trace organic contaminant removal from wastewater of a resort town: comparison between a pilot and a full scale membrane bioreactor. International Biodeterioration and Biodegradation, 102 40-48.

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International Biodeterioration & Biodegradation
February, 2015; http://dx.doi.org/10.1016/j.ibiod.2015.02.010

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Highlights

- 41 TrOCs were identified at levels above the detection limit in raw sewage
- The full-scale MBR showed better nutrient and TrOC removal than the pilot-scale MBR.
- Multiple anoxic/aerobic reactors promoted removal of nutrients and some TrOCs
- Removal of eight of the monitored TrOCs closely followed the TN removal profile
- MBR effluent complied with the water reuse guideline for all but three TrOCs

Abstract
The occurrence of a broad spectrum of trace organic contaminants (TrOCs) in raw sewage from a small resort town and their removal by a full- and a pilot-scale membrane bioreactor (MBR) was analysed in this study. The MBR systems demonstrated similar reduction of chemical oxygen demand. However, the full-scale MBR sustained higher and more stable nutrient removal (>95% for both total nitrogen, TN and phosphate, PO_4^{3-}-P) than the pilot-scale system (*ca.* 80% TN and 30% PO_4^{3-}-P removal). Of the 45 monitored TrOCs including pharmaceuticals and personal care products (PPCPs), industrial chemicals, steroid hormones, and pesticides, 41 compounds were detected in the raw sewage above detection limits of 5-20 ng L^{-1}. A correlation between the removal of TN and eight TrOCs (atenolol, caffeine, naproxen, ibuprofen, gemfibrozil, DEET, estrone and diuron) was observed. Additionally, the full-scale MBR demonstrated higher and/or more stable removal for sulfamethoxazole, trimethoprim, diclofenac, diuron and amitriptyline. With the exception of caffeine, estrone and triclosan, TrOC concentrations in MBR effluent were lower than the Australian Guidelines for Water Recycling: Augmentation of Drinking Water Supplies.

Keywords: trace organic contaminants (TrOCs); membrane bioreactor; nutrient removal; decentralised WWTP; water reuse.

1. Introduction

Increasingly stringent environmental regulations and freshwater shortages are key drivers for a worldwide trend to introduce advanced sewage treatment infrastructure for removing nutrients (i.e., nitrogen and phosphorous) and trace organic contaminants (TrOCs) along with the bulk organics. In particular, due to the ineffectiveness of conventional secondary wastewater treatment processes, TrOCs such as pharmaceuticals and personal care products (PPCPs), industrial chemicals, steroid hormones and pesticides are ubiquitous in wastewater treatment plant (WWTP) effluents. Ineffective wastewater treatment is a major conduit by which TrOCs reach natural water bodies. This raises considerable concern regarding their effects on the aquatic organisms and even humans after chronic ingestion (Luo et al., 2014).

Small to medium WWTPs are being progressively implemented in small townships and tourism hot spots around Australia to phase out unreliable septic tank systems. Several studies have assessed the occurrence of TrOCs in wastewater originating from various catchment areas including agricultural, rural, urban and industrial wastewater catchments (Leusch et al., 2014; Scott et al., 2014) and the treated effluent produced by various types and scales of WWTPs (Coleman et al., 2008; Leusch et al., 2014; Ying et al., 2009). However, only a few studies reported the TrOC profile of raw sewage generated from small Australian towns (Braga et al., 2005; Coleman et al., 2008; Leusch et al., 2014), particularly those which are tourist destinations (Le-Minh et al., 2010; Trinh et al., 2012b). Wastewater from small resort towns can have distinct characteristics in terms of volume of wastewater produced and also the frequency and concentration in which TrOCs may occur. A majority of the Australian studies investigated the removal efficiency of WWTPs for endocrine disrupting chemicals, particularly the steroid hormones, with fewer studies also focusing on pharmaceuticals, industrial chemicals and pesticides (Le-Minh et al., 2010; Trinh et al., 2012a). Notably most available reports on TrOC removal from real sewage have documented the performance of conventional treatment technologies (e.g., activated sludge process, biofilters, and lagoons) (Ying et al., 2009).

Membrane bioreactors (MBRs) are an attractive option for decentralised wastewater treatment and reuse due to their ability to produce high quality effluent with a small footprint (Hai et al., 2014). MBRs account for the majority of new sewage treatment infrastructure in Australia. Most of these are small to medium MBR plants for water recycling applications in coastal towns and small cities, and are mostly driven by stringent environmental regulations, particularly targeting nutrient and TrOC removal, and to a lesser extent by freshwater scarcity. To date only a few Australian studies have investigated TrOC removal from real sewage, and these studies have been conducted mostly via pilot-scale MBRs (Coleman et al., 2008; Le-Minh et al., 2010; Trinh et al., 2012b). Available studies provide useful preliminary understanding; however, the performance of current MBR technology as a barrier for a range of TrOCs and specific removal mechanisms involved remains unclear.

Biodegradation can proceed under aerobic, anoxic or anaerobic regimes. Sequential exposure to different redox conditions is a pre-requisite to nutrient (i.e., nitrogen and phosphorus) removal from wastewater. For example, nitrogen removal occurs via nitrification under aerobic conditions and denitrification under anoxic conditions. In order to achieve high nitrogen removal, complete nitrification and effective recirculation of nitrate to the anoxic zones is necessary. A simple two-stage pre-anoxic/aerobic reactor configuration can typically meet the total nitrogen (TN) disposal guideline of 10 mg L^{-1} (Hai et al., 2014). A series of aerobic/anoxic zones with supplemental organic carbon dosing to the anoxic zone may be required to achieve further improved TN removal to comply with a more stringent effluent

TN guideline (sensitive areas). This may also facilitate stable removal when TN loading in wastewater fluctuates significantly. Notable in this context is that recent studies demonstrate close relationships between stable NH_4^+-N removal and the removal of TrOCs (Helbling et al., 2012). Most of the previous reports have shown the correlation of TrOC removal with the stability of NH_4^+-N removal via batch tests conducted with synthetic wastewater. Other than the only study by Vader et al. (2000) who showed a noticeable connection between NH_4^+-N and 17α- ethinyl estradiol removal, this correlation has not been validated at full scale level. Furthermore, compared with aerobic (nitrifying) conditions, fewer studies have investigated TrOC removal performance of combined anoxic/aerobic reactors (Phan et al., 2014; Xue et al., 2010). It is not clear whether, like TN, a combination of a number of aerobic and anoxic zones with different levels of dissolved oxygen concentration (DO) may be conducive to removal of different TrOC categories.

Given the research gaps discussed above, the aim of this study was to assess the occurrence and removal of a broad spectrum of TrOCs by a full-scale MBR plant serving a small resort town. Performance comparison with a pilot-scale MBR fed with the same sewage was used to clarify important aspects regarding bulk organics, TrOCs and nutrient removal. The potential impact of the application of multiple sequences of anoxic/aerobic regimes on nutrient and TrOC removal is also discussed.

2. Materials and Methods

This study was conducted at a full-scale MBR plant (designed for a maximum capacity of 743 m^3 d^{-1}) located in Kangaroo Valley (New South Wales, Australia), which is a tourist destination known for caravan parks. The Kangaroo Valley township has a permanent population of about 340 people; however, this increases during peak holiday periods to approximately 1400. In addition to influent wastewater sampling over 15 events (from November 2012 to October 2014), a pilot-scale MBR was operated at the site. It was first operated for 11 weeks for acclimatization and performance stabilization. Then, a 10-week sampling campaign was carried out to compare the treatment performance of the pilot- and full-scale MBRs receiving the same sewage.

2.1 Description of the full-scale MBR

The MBR received wastewater via a pressurised sewerage network from the Kangaroo Valley township. A schematic diagram of the plant is presented in Supplementary Data Figure 1. The treatment process comprised i) primary treatment, ii) two parallel trains of activated sludge reactors integrated with membrane filtration cells, and iii) a UV disinfection unit (UV dose of 40 mJ/cm^2). One of the duplicate process trains was operated in stand-by mode. The activated sludge system consisted of a pre-anoxic zone (DO = 0-0.5 mg L^{-1}), aerobic zone-1 (DO = 0.5-1.0 mg L^{-1}), aerobic zone-2 (DO = 2-2.5 mg L^{-1}), and a post-anoxic zone (DO = 0-0.5 mg L^{-1}) receiving supplemental organic carbon (acetic acid, approximately 40 L d^{-1}) to enhance denitrification. The mixed liquor from the aerobic zone-2 was recycled to the pre-anoxic zone with an internal recirculation ratio of 4. The return activated sludge from the membrane cell was recycled to aerobic zone-2 and the pre-anoxic zone, also with a recirculation ratio of 4. The solids retention time (SRT) of the MBR was 25 d and the mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) concentration in the aerobic reactors were respectively 8.5 ± 0.7 and 6.2 ± 0.5 g L^{-1} (n=10) during the period of performance-comparison with the pilot MBR. The total hydraulic retention time (HRT) was 1.5 - 1.7 d with approximate HRTs in pre- anoxic zone, aerobic zone-1, aerobic zone-2, post-anoxic zone and the membrane cell of 0.45, 0.45, 0.45, 0.22 and 0.14 d, respectively. PVDF

microfiltration membranes (Memcor, Evoqua Water Technologies, Australia) were submerged into the membrane cells to provide a surface area of 2400 m^2/cell.

During the course of this study, the total sewage flowrate was 146 ± 76 m^3 d^{-1} (n = 66), and the membrane flux was 2.1 ± 1.1 (n = 66) and 1.1 ± 1.1 L m^{-2} h^{-1} (n = 31) for the primary and stand-by membrane cells, respectively. The final effluent was directed to a storage dam and then used for irrigation to farms and recreational facilities around the region.

2.2 Pilot-scale MBR setup and operation

A pilot-scale anoxic-aerobic MBR (Supplementary Data Figure 1) was operated parallel to the full-scale MBR. The pilot MBR was operated under the same SRT (25 d), total HRT (1.5 d) and with the same internal recirculation ratio (4) between anoxic-aerobic reactors. However, compared to the four reactors (2 x anoxic and 2 x aerobic) in the full-scale MBR, it contained only one pre-anoxic zone (working volume= 13.8 L, HRT= 0.8 d) and an aerobic zone (working volume= 11.7 L, HRT= 0.7 d). A hollow fibre ultrafiltration membrane (Zeweed-10) supplied by Zenon Environmental (Ontario, Canada) was submerged in the aerobic reactor. This membrane had a nominal pore size of 0.04 µm and an effective membrane surface area of 0.93 m^2, and was operated at a flux of 1.2 L m^{-2} h^{-1}. The transmembrane pressure (TMP) was continuously recorded via a high resolution (±0.1 kPa) pressure sensor connected to a data logging computer. All pumps were controlled via the same computer. The computer was remotely controlled over the internet using the TeamViewer software. Throughout the whole experimental period, *in-situ* air scrubbing was found adequate to keep the TMP stable below 5 kPa, and no chemical cleaning was required. The mixed liquor pH was stable at 7.14 ± 0.35 (n = 14) and 7.43 ± 0.45 (n = 14) for the anoxic and aerobic bioreactors, respectively. DO was maintained in the range of 2.5 – 5 mg L^{-1} for the aerobic zone and 0 - 0.25 mg L^{-1} for the anoxic zone. The temperature inside the bioreactors varied according to the ambient temperature at 18 ± 3 ^oC. MLSS and MLVSS concentrations of the anoxic reactor were 4.1 ± 0.5 and 2.7 ± 0.3 g L^{-1} (n=18), respectively, with the corresponding values (n=18) of 2.4 ± 0.8 (MLSS) and 1.5 ± 0.6 (MLVSS) g L^{-1} for the aerobic bioreactor.

2.3 Sample collection and analysis

2.3.1 Sample collection

Amber glass bottles (500 mL) pre-rinsed with Milli-Q water were used for sample collection. Grab sewage samples (35) after primary settling (Supplementary Data Figure 1) were collected over 15 sampling events to characterize the sewage originated from Kangaroo Valley. These influent samples were collected in duplicate (first 10 sampling events) or triplicate (last five sampling events) from November 2012 to October 2014 and analysed for both bulk organics and TrOCs. On the other hand, following the 11-week acclimatization period of the pilot MBR, effluent samples from the pilot- and full-scale MBRs along with the influent samples were collected to compare their performance over a period of 10 weeks. TrOC removal by the pilot- and full-scale MBRs was monitored during the last six week of sampling.

2.3.2 Analysis of basic parameters

Total organic carbon (TOC) and total nitrogen (TN) were analysed using a TOC/TN-V_{CSH} analyser (Shimadzu, Japan). Chemical oxygen demand (COD) was analysed using COD vials (0-1500 ppm, WatertestSystems, Australia) with a Hach DR 5000 spectrophotometer according to the Standard Method 5220 D (Eaton et al., 2005). NH_4^+-N and ortho- PO_4^{3-}-P concentrations were measured using flow injection analysis (Lachat instruments, Milwaukee,

USA) following the Standard Methods 4500-NH_3 H and 4500-P G, respectively (Eaton et al., 2005). MLSS and MLVSS concentrations in bioreactors were measured according to the Standard Method 2540 (Eaton et al., 2005).

2.3.3 Trace organic contaminant analysis

In total, 45 TrOCs including 27 PPCPs, four industrial chemicals, eight steroid hormones and six pesticides were monitored in this study. Influent and MBR effluent samples (0.5 L) were collected and immediately transferred to the laboratory. The influent samples were filtered through 1 µm and then 0.45 µm glass fibre filters (Millipore, Australia), but the membrane-permeate samples were not further filtered. Concentrations of TrOCs were determined by solid phase extraction (Oasis HLB, Waters, Millford, MA, USA) followed by analysis using high performance liquid chromatography (Agilent 1200 series, Palo Alto, CA, USA) coupled with tandem triple quadrupole mass spectrometer (API 4000, Applied Biosystems, Foster City, CA, USA) employed in both positive and negative electro-spray modes and atmospheric pressure chemical ionization in positive mode. Isotope dilution was used to quantify all analytes unless otherwise stated. The detailed method is available in Supplementary Data Table S2.

2.3.4 Statistical analysis of data

Average ± standard deviation values were used to compare the concentrations and removal/reduction efficiency of different parameters namely, TOC, COD, TN, NH_4^+-N and PO_4^{3-}-P. Distributions of TrOC concentrations were analysed in terms of maxima, minima, 95th and 5th percentiles and the median. Paired *t*-test of the TrOC removal data (pilot- vs full-scale MBR) was conducted using the *t*-test function in Microsoft Excel. Values of $p < 0.05$ were considered to indicate statistical significance.

3. Results and discussion

3.1 Bulk organics removal

To assess the bulk organics removal by the pilot- and full-scale MBRs, both TOC and COD were analysed. During the period of comparison (Days 77–146), the influent TOC was 68 ± 25 mg L^{-1} (n = 10). The effluent TOC concentration for the pilot- and the full-scale MBR varied in the range of 21 ± 14 and 30 ± 15 mg L^{-1}, respectively (Figure 1). The removal efficiency was 68 ± 15% for the pilot-scale MBR and 52 ± 22% for the full-scale MBR. On the other hand, the influent COD varied in the range (n = 10) of 156 ± 91 mg L^{-1} (Supplementary Data Figure 2). The range of effluent COD concentration was 25 ± 15 (pilot-scale MBR) and 19±6 (full-scale MBR) mg L^{-1}. Accordingly, the removal efficiencies were 78 ± 17% and 82 ± 14% for the pilot- and full-scale MBRs, respectively.

[Figure 1]

External carbon source (acetic acid) was added to the post-anoxic reactor of the full-scale MBR to enhance denitrification. Over-addition of carbon may, however, leave excess carbon in the effluent (Chou et al., 2003). This may explain the somewhat lower TOC removal by the full-scale MBR (Figure 1). Conversely, the COD removal efficiency of the MBRs was rather similar (Supplementary Data Figure 3), indicating that TOC is a more sensitive parameter to capture variations in bulk organics removal performance.

3.2 Nutrients removal

During the period of comparison (Days 77–146), the influent TN varied significantly in the range of 39 ± 19 mg L^{-1}, while the effluent TN was 17 ± 21 and 2 ± 1 mg L^{-1} (n = 10) for the pilot- and full-scale MBRs, respectively (Figure 1). Thus the TN removal efficiency varied in the range of 62 ± 28% (pilot-scale MBR) and 94 ± 5% (full-scale MBR). The data demonstrate a high and stable TN removal by the full-scale plant that is significantly better than that of the pilot-scale MBR. The pilot-scale MBR comprised a pre-anoxic zone and an aerobic zone (Supplementary Data Figure 1). It is noted that a complete denitrification may not be achieved by this configuration since part of the aerobic effluent is not recycled through the anoxic zone (Phan et al., 2014). The full-scale MBR utilized a four-stage nitrogen removal configuration (two aerobic zones plus pre-and post-anoxic zones) where the second anoxic zone provides for additional denitrification using remaining nitrate produced from aerobic stages as electron acceptor and external carbon source as the electron donor (Hai et al., 2014). Thus, despite significant variations in influent TN, the full-scale plant achieved an effluent TN concentration of 2 ± 1 mg L^{-1}, which is considered the typical level of refractory dissolved organic nitrogen in wastewater treatment plant effluent (Hai et al., 2014).

[Figure 2]

Both MBRs were observed to achieve complete nitrification. That is the NH_4^+-N concentration in the effluent being below the detection limit of the method of analysis (Figure 2). This is consistent with the excellent NH_4^+-N removal achieved in another study involving a decentralised full-scale MBR plant (Trinh et al., 2012b). However, consistent with the case of TN removal, the full-scale MBR showed a more stable NH_4^+-N removal performance. This could again be attributed to the four-reactor configuration, particularly the existence of two aerobic zones in the full-scale MBR. The higher MLVSS concentration (approximately four-fold, see Materials and Methods) in the full-scale MBR may be another reason for such stable performance. The pilot-scale MBR was not designed for PO_4^{3-}-P removal; hence, as shown in Figure 2, the system achieved only marginal PO_4^{3-}-P removal performance (31 ± 15%, n =10). By contrast, the full-scale MBR exhibited high and stable PO_4^{3-}-P removal (98 ± 4%, n = 10). This excellent PO_4^{3-}-P removal can be explained by the higher MLVSS concentration and the combination of additional anoxic and aerobic bioreactors in the full-scale MBR.

3.3 Occurrence of TrOCs in influent wastewater

There are only a few studies reporting the TrOC profile of raw sewage generated from small towns in Australia (Le-Minh et al., 2010; Leusch et al., 2014; Scott et al., 2014; Trinh et al., 2012b). Thus a critical discussion regarding the frequency and concentration of the TrOCs detected in the influent wastewater is necessary to facilitate assessment of the TrOC removal capacity of the MBRs. Of the 45 monitored TrOCs (27 PPCPs, eight steroid hormones, four industrial chemicals and six pesticides), all except three pharmaceuticals (dilantin, risperidone and hydroxyzine) and one pesticide (linuron) were detected in the raw sewage samples at a wide range of concentrations above the detection limit (5–20 ng L^{-1}, depending on the compound, see Supplementary Data Table S4). High variability in the concentration of some TrOCs (Figure 3) may be explained by the fact that Kangaroo Valley has a permanent population of only 340, and this number can be tripled in peak holiday periods.

[Figure 3]

Among the PPCPs, caffeine was detected in all samples and with the greatest maximum TrOC concentration (140 µg L^{-1}) observed in raw sewage in this study (Figure 3). The common

sources of caffeine are coffee, tea, soft and energy drinks, and caffeine supplements (stimulants), which explain why it is usually detected at high concentration in raw sewage (Luo et al., 2014). However, it is noteworthy that the maximum caffeine concentration detected in the current study is about 3.5 times higher than the value reported for raw sewage from a similar wastewater catchment in Australia (Trinh et al., 2012b) and significantly higher than the values reported overseas (Luo et al., 2014). Given its extensive consumption in Australia (PBS/DH, 2014), the high concentration of paracetamol (maximum detected concentration of 130 µg L^{-1}) observed in this study was not a surprise. Notably, non-prescription drugs were detected much more frequently and at greater concentrations. For example, anti-inflammatory drugs ibuprofen, diclofenac and naproxen were detected in all 35 samples and at concentrations up to three orders of magnitude higher than the prescription anti-inflammatory drug ketoprofen (Figure 3). The maximum concentration (5.8 µg L^{-1}) of the antihypertensive drug atenolol was similar to that reported previously (Trinh et al., 2012b). Notable, however, is that unlike the rest of the antihypertensive drugs (i.e., enalapril, verapamil, triamterene), atenolol was detected in all samples and showed concentrations up to two orders of magnitude higher than the rest. This can be attributed to extensive use of atenolol in Australia for cardiovascular diseases (PBS/DH, 2014). The impact of usage-mode on the detected concentration was also noted in case of the two antibiotics sulfamethoxazole and trimethoprim – these antibiotics are often used in combination, for example, in 5:1 ratio, which may explain the significantly higher concentration of sulfamethoxazole detected in this study. Other prescription drugs detected frequently and at significant concentrations included the antilipidemic drug gemfibrozil (11–730 ng L^{-1}), the antidepressants fluoxetine (8 – 130 ng L^{-1}) and amitriptyline (7 – 480 ng L^{-1}), and the antiepileptic drugs carbamazepine (8 – 700 ng L^{-1}) and primidone (12 – 170 ng L^{-1}). The median age of the Kangaroo Valley population is 48 years, which is 11 years above the Australian average (ABS, 2011). This feature may have contributed to high consumption of prescription drugs in this area.

Ingredients of personal care products (i.e, triclosan, triclocarban, polyparaben and DEET) were frequently detected in the Kangaroo Valley raw sewage. For example, triclosan and triclocarban, which are antimicrobial agents used in toiletries, were detected in all samples and at maximum concentrations consistent with a previous study (Trinh et al., 2012b), although with significant week to week variation (concentration ranges of 60 -1300 ng L^{-1} and 15 – 1000 ng L^{-1} for triclosan and triclocarban, respectively). A similar behaviour was noted in case of polyparaben (a preservative used in cosmetics), which was detected at a wide concentration range of 56 – 3300 ng L^{-1} (Figure 3). However, DEET (an active ingredient of most commercial insect repellents) was detected at a relatively narrow concentration range of 1.5 – 11.3 µg L^{-1} – the maximum value surpassing the previously reported ones (Trinh et al., 2012b). Notable in this connection that two samples analysed with a different method probing some additional TrOCs confirmed few tens of microgram per litre of octocrylene and benzophenone (ingredients of UV filters) and salicylic acid –an ingredients in medicinal/cosmetic products (data not shown).

Consistent with the rural nature of the area, the industrial xenoestrogens bisphenol A (21 – 270 ng L^{-1}, n= 12) and 4-n-nonylphenol (25 – 70 ng L^{-1}, n=5) were detected with concentrations at the lower end of the previously reported values in Australia (Scott et al., 2014; Tan et al., 2007; Trinh et al., 2012b). TCEP, a flame retardant commonly found in products such as foams and plastics, was detected more frequently but at a concentration range of 23 ± 11 ng L^{-1} (n = 25), except for one sample with a high concentration of 300 ng L^{-1}. No Australian reports could be retrieved for comparison, but this TCEP concentration range

is significantly lower than the few wastewater TCEP data available from Europe (Luo et al., 2014; van der Veen and de Boer, 2012).

All eight monitored steroid hormones were detected in the raw sewage (Figure 3). Among the androgenic hormones (i.e., testosterone, etiocholanolone and androsterone), the primary male sex hormone testosterone was detected at low concentrations (<5 – 14 ng L^{-1}), while its metabolites (i.e., etiocholanolone and androsterone) occurred at much higher concentrations (1.1 – 5.8 µg L^{-1} and 0.27 – 0.98 µg L^{-1}, respectively) and with greater frequency (Figure 3). This is in accordance with previous studies (Tan et al., 2007; Trinh et al., 2012b). The estrogen 17β-estradiol and its natural epimer 17α-estradiol were detected in low concentrations (7 – 54 ng L^{-1} and 5 – 14 ng L^{-1}, respectively). 17β-estradiol is the predominant estrogen during reproductive years, however, in wastewater this can swiftly degrade to estrone (Coleman et al., 2009), which can explain the high concentration of estrone (up to 0.75 µg L^{-1}) detected in this study (Figure 3). However, the maximum estrone concentration observed in this study was about seven times higher than the values reported for Australian sewage previously (Coleman et al., 2009; Trinh et al., 2012b). The extremely small sewage catchment area is the most likely reason of such high variability and unusual results. However, it is interesting to note that estrone is the predominant estrogen in postmenopausal women, which matches the demography of the study area. Notable also in this connection is the fact that estriol, which is associated with pregnancy, was detected at a high concentration of 1.7 µg L^{-1} but only during one sampling event (n = 3) which coincides with a peak holiday period, indicating that this possibly came from the tourists.

Pesticides are hardly biodegradable TrOCs (Hai et al., 2012). Except linuron, all other pesticides monitored (i.e., atrazine, diazinon, simazine, phenylphenol and diuron) were detected in the raw sewage at different concentrations. Among these, diuron was detected frequently and at a concentration of up to 0.7 µg L^{-1} (Figure 3), which is higher than the values reported in a recent Australian study covering a few selected urban and rural wastewater treatment plants (Leusch et al., 2014). Diuron is used extensively in Australia for the control of weeds in certain crops (e.g., wheat, barley and sugarcane) and thus frequently detected in surface water. Its application to control a wide variety of broadleaf and grassy weeds along the roads and garden paths could be the source for their occurrence in Kangaroo Valley raw sewage.

3.4 Overall TrOC removal by the MBRs

Significantly hydrophobic compounds (approximately possessing a log *D* over 3) are generally well removed from the aqueous phase via sorption to biosolids. Depending on their biodegradability, the biosorbed TrOCs may be further degraded. In this study, the steroid hormones (log $D_{pH=8}$ = 3.62 – 3.93) were efficiently removed by the MBRs (Figure 4). Similar removal from real wastewater has been reported for the steroid hormones in previous studies (Le-Minh et al., 2010; Trinh et al., 2012a). Furthermore, none of these TrOCs were detected in sludge (Supplementary Data Table S5), evidencing their high biotransformation. Halogenated personal care products triclosan and triclocarban possess high hydrophobicity (log $D_{pH=8}$ of 4.93 and 6.07, respectively), and were significantly removed from the aqueous phase. However, their high resistance to biodegradation (Hai et al., 2011b) was evident as triclosan and triclocarban were detected in pilot-MBR sludge at a concentration of 190 – 230 and 790 – 1100 ng g^{-1}_{MLSS}, respectively.

[Figure 4]

The MBRs achieved high and stable removal (>90%) of eight PPCPs (atenolol, caffeine, naproxen, ibuprofen, paracetamol, gemfibrozil, DEET and propylparaben). These compounds are hydrophilic (log $D_{pH=8} < 3$), and thus biodegradation is thought to be the major removal mechanism during biological treatment processes. These PPCPs are generally characterized as significantly biodegradable (Trinh et al., 2012b; Xue et al., 2010), although the removal of some compounds such as naproxen and DEET has been observed to be variable (Tadkaew et al., 2011). However, the MBRs showed little removal of the anticonvulsant drugs carbamazepine and primidone. Both compounds contain strong electron withdrawing amide groups, while primidone additionally contains a weak electron donating group (methyl). Occurrence of strong electron withdrawing groups and/or absence of electron donating groups impart resistance to biodegradation (Tadkaew et al., 2011). Indeed these TrOCs, particularly carbamazemine, have been widely reported to be resistant to biodegradation (Le-Minh et al., 2010; Tadkaew et al., 2011; Trinh et al., 2012b). A few resistant compounds (i.e., sulfamethoxazole, trimethoprim, diclofenac and diuron), which were detected at high concentrations in the raw sewage, were better removed by the full-scale plant ($p<0.05$, see Supplementary Data Table S6). This aspect is discussed in further detail in a following section.

It is important to note here that of the 35 raw sewage samples collected over 15 sampling events (Figure 3), TrOC removal estimation has been based on 12 samples (duplicate samples once a week over six weeks) for which the corresponding treated effluent samples were available. However, except for paracetamol, the median influent TrOC concentrations were the same for both sets of data (Supplementary Data Table S7), indicating that the TrOC removal efficiencies reported in this study can be considered a reasonable representation of the full-scale plant capacity.

3.5 Correlation between TN and TrOC removal

Of the six weeks of TrOC removal comparison (Days 105– 46), on the 2nd to 5th week, the wastewater NH_4^+-N and TN concentrations fluctuated significantly (TN concentration of 50, 75, 20, and 60 mg L^{-1} in samples measured on days 112, 119, 127 and 133, respectively), leading to low NH_4^+-N (Figure 2) and TN (Figure 5) removal. Notably, as the influent TN leaped from 49 (on Day 112) to 76 mg L^{-1} on Day 119, an immediate drop in removal of eight TrOCs, namely, atenolol, caffeine, naproxen, ibuprofen, gemfibrozil, DEET, estrone and diuron by the pilot MBR was observed (Figure 5). Furthermore, the removal-profile of some of these TrOCs continued to closely follow the rise and fall in the (NH_4^+-N and) TN removal profile. By contrast, the full-scale MBR TN removal was little impacted by the fluctuation in TN concentration (Supplementary Data Figure S8). TrOC removal (except that of atenolol on Day 119) by the full-scale MBR also remained stable (Supplementary Data Figure S8) during the period of TN fluctuation in influent. Previous studies have shown a close relationship between stable NH_4^+-N removal and the removal of many TrOCs including atenolol (Helbling et al., 2012), ibuprofen and naproxen (Fernandez-Fontaina et al., 2014), and gemfibrozil (Maeng et al., 2013). Also DEET was shown to be metabolized only in the presence of nitrogen (Rivera-Cancel et al., 2007). Of particular relevance to the observed drop in TrOC removal due to rise in influent NH_4^+-N concentration is the study of De Gusseme et al. (2009) who showed that nitrifying cultures may preferentially oxidize ammonia rather than the synthetic estrogen 17α-ethinyl estradiol under elevated NH_4^+-N concentration. Most of the previous reports showing an association of TrOC removal with the stability of NH_4^+-N and TN removal were conducted with synthetic wastewater via batch tests. By contrast, this study

shows the link between stable TN and TrOC removal via unique results from the pilot- and full-scale MBRs fed with the same raw sewage.

[Figure 5]

3.6 Better TrOC removal by full-scale MBR: possible reasons

The full-scale MBR showed significantly better removal of four hydrophilic TrOCs namely, the pharmaceuticals sulfamethoxazole, trimethoprim and diclofenac, and the pesticide diuron. Additionally, in contrast to no removal by the pilot-scale MBR, a moderate removal of the antidepressant drug amitriptyline was achieved by the full-scale MBR (Figure 4). Amitriptyline is a significantly hydrophobic compound (log $D_{pH=8}$ = 3.21), and due to its persistence in sludge, its removal by MBR has been attributed mainly to biosorption (Tadkaew et al., 2011; Trinh et al., 2011). Significant variability in amitriptyline removal, as observed in the current study as well as in previous work (Tadkaew et al., 2011; Trinh et al., 2011; Trinh et al., 2012b), may be attributed to the biosorption capacity, which may be site- and MBR-design (e.g., anoxic/aerobic sequences applied)-specific. Among the hydrophilic TrOCs, sulfamethoxazole has been shown to undergo biodegradation under a range of redox conditions, particularly at low DO (Hai et al., 2011a; Stadler et al., 2015), which were the conditions in the first aerobic reactor in the full-scale MBR. Conversely, to date the biodegradation of the resistant TrOC diclofenac has been shown to occur only under stable nitrifying conditions (Vieno and Sillanpää, 2014), as was also achieved by the full-scale plant. A few reports additionally indicate that a delicate combination of aerobic and anoxic conditions such as that in attached growth systems may favour diclofenac degradation (Vieno and Sillanpää, 2014; Zwiener and Frimmel, 2003) – it is possible that in the current study the full-scale MBR had facilitated such redox conditions. Similarly, the excellent removal of diuron (98 ± 3%) by the full-scale MBR was possibly facilitated by the combination of different redox zones as also suggested by Stasinakis et al. (2009).

Higher removal of the hydrophilic TrOCs by the full-scale plant (i.e., sulfamethoxazole, trimethoprim, diclofenac, and diuron) or more stable removal of other TrOCs (as discussed in the previous section) may be attributed to the existence of pre- and post-anoxic tanks, and combination of aerobic zones with different levels of DO as compared to a pre-anoxic and a single aerobic tank in the pilot MBR. For a clearer understanding, further studies specifically on different combinations of anoxic and aerobic reactors for TrOC removal by MBR are recommended.

Direct UV photolysis of TrOCs can occur at elevated dosages (Nguyen et al., 2013), but a significant body of literature has shown that at disinfection dosages direct UV photolysis is ineffective in removing most TrOCs (Yang et al., 2013). Thus, it is unlikely that better removal by the full-scale MBR compared to the pilot MBR observed here was due to full-scale effluent sample being collected after the UV disinfection unit.

[Table1]

Because TrOC concentrations in the raw sewage varied significantly (Figure 3 and Supplementary Data Table S7), in addition to monitoring the removal efficiency, the effluent TrOC concentrations were compared with the Australian Guidelines for Water Recycling: Augmentation of Drinking Water Supplies (NRMMC/EPHC/NHMRC, 2008). The full-scale plant effluent was intended only to be reused in irrigation. However, comparing the effluent quality against these guidelines further facilitate the performance-comparison of the pilot- and full-scale MBRs. For example, caffeine usually registered a removal of 95 – 99% by the

MBRs (Figure 4); however, when it was detected in the influent at the maximum concentration (138 µg L^{-1}), the pilot MBR effluent concentration (51.5 µg L^{-1}), but not that of the full-scale MBR effluent, exceeded the guideline value of 3.5 µg L^{-1} (Table 1). Compared to caffeine, estrone was detected at much lower influent concentrations (0.005 – 0.80 µg L^{-1}) and estrone removal was consistently over 95%. Thus, with only one exception, the pilot MBR effluent complied with the Australian Guidelines for Water Recycling: Augmentation of Drinking Water Supplies (NRMMC/EPHC/NHMRC, 2008) despite the fact that a much stricter guideline value has been imposed for estrone (0.03 µg L^{-1}). By contrast, because triclosan removal varied from 35 to 95% (Figure 4), a third of the effluent samples (both MBR system) could not comply with the moderate guideline value of 0.35 µg L^{-1} (Table 1). Interestingly, despite low removals of carbamazepine, diuron and amitriptyline by the pilot MBR (Figure 4), their effluent concentrations were within the limit of guideline values (Table 1). MBR-effluent TrOC concentrations observed in this study are consistent with that from the literature (Coleman et al., 2009; Trinh et al., 2012b). However, via the performance-comparison between the pilot- and full-scale MBRs, this study offers unique insight into the impact of application of multiple anoxic/aerobic treatment sequences on TrOC removal and compliance to water reuse guidelines.

4. Conclusions

To address a notable omission in the literature, this study analysed nutrient and TrOC removal performance by a full- and a pilot-scale MBR from wastewater originating from a resort town and showing significant fluctuations in concentrations of the target pollutants over time. The pilot-scale MBR demonstrated a very similar COD reduction as the full-scale MBR. Given the significantly higher MLVSS concentration and presence of additional anoxic and aerobic bioreactors in the full-scale plant, the removal of nutrients, particularly that of phosphorous by the full-scale MBR was significantly high (98 ± 4% vs. 31 ± 15% PO_4^{3-}-P removal by the pilot-scale MBR). Notably, any drop in TN or NH_4^+-N removal by the full-scale MBR was accompanied by a drop in the removal by the pilot-scale MBR, although the full-scale plant appeared to be more stable under influent load fluctuations. The full-scale MBR demonstrated higher and more stable removal of a few resistant and hydrophilic (log D < 3) TrOCs including sulfamethoxazole, trimethoprim, diclofenac and diuron. Performance comparison between the pilot- and full-scale MBRs reveals a link between stable TN and TrOC removals which were facilitated by a delicate combination of redox zones in the bioreactors.

Acknowledgments

Hop V. Phan has been supported by a PhD scholarship from the University of Wollongong, Australia and the Thanh Hoa provincial government, Viet Nam. Zenon Environmental Inc., Canada is thanked for supplying the membrane module for the pilot MBR. A UOW Research Partnership Grant with Shoalhaven Water is gratefully acknowledged. Dr. Samia Shawkat of the Illawarra Health and Medical Research Institute, University of Wollongong is thanked for valuable advice on the classification and therapeutic functions of the pharmaceuticals investigated. Thanks are due to Luke Elliott – the operator of the Kangaroo Valley full-scale MBR plant – for his kind cooperation throughout the study period.

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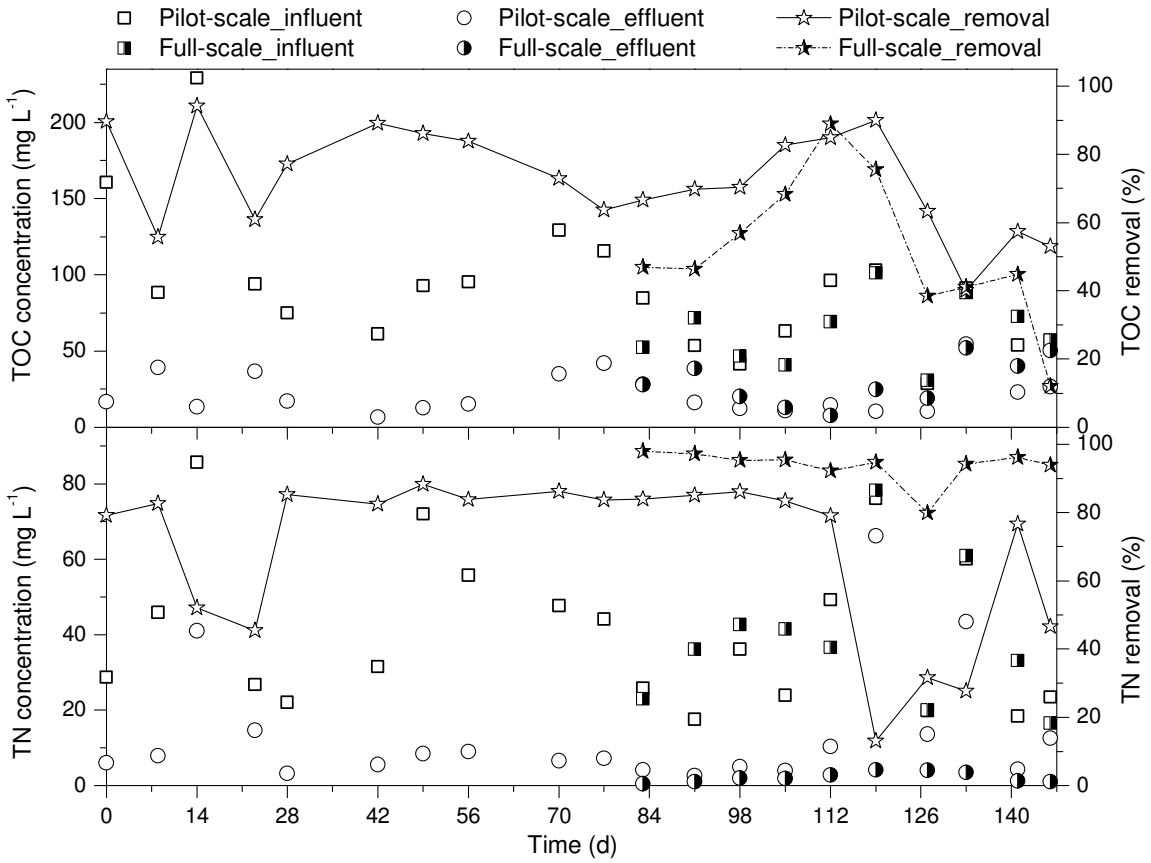
List of Tables

Table 1: Concentrations of TrOCs detected in the permeate from the pilot- and full-scale MBRs and the Australian guideline values for augmentation of drinking water supplies (NRMMC/EPHC/NHMRC, 2008). Data presented as 'concentration range (median value)'.

Compounds	Concentration of TrOCs (ng L^{-1})		
	Pilot-scale MBR effluent	Full-scale MBR effluent	Australian guideline values
Atenolol	34 - 1700 (58)	42 - 210 (88)	Not available[a]
Sulfamethoxazole	<5 - 1700 (48)	<5 - 310 (49)	35,000
Caffeine	60 - 55800 (220)	31 - 230 (68)	35,00
Naproxen	35 - 1100 (250)	<5 - 290 (33)	220,000
Ibuprofen	<5 - 1400 (38)	<5 - 400 (45)	400,000
Paracetamol	<5	<5	175,000
Trimethoprim	13 - 490 (40)	20 - 210 (71)	70,000
Primidone	<5 - 180 (25)	<5 - 840 (27)	Not available
Diclofenac	87 - 270 (193)	<5 - 180 (87)	1800
Gemfibrozil	<5 - 80 (<5)	<5 - 20 (11)	600,000
Carbamazepine	270 - 660 (330)	330 - 600 (454)	100,000
DEET	50 - 4200 (165)	<5 - 31 (12)	2,500,000
Diuron	<10 - 180 (17.6)	<10 - 190 (<10)	30,000
Polyparaben	<10	<10	Not available
Amtriptyline	53 - 260 (89)	40 - 99 (60)	70,000
Triclosan	47 - 1200 (180)	14 - 730 (160)	350
Triclocarban	<10 - 38 (<10)	<10 -46 (34)	Not available
Estriol	<5	<5	50
Androstenedione	<5	<5	Not available
Testosterone	<5	<5	7000
Estrone	<5 - 82 (<5)	<5	30
17β-estradiol	<5	<5	175
17α-estradiol	<5	<5	175
Androsterone	<5	<5	14,000
Etiocholanolone	<5	<5	Not available

Note: [a]Values for other β-blockers are 350-40,000

List of Figures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Pilot-scale_effluent
Pilot-scale_removal
Full-scale_influent
Full-scale_effluent
Full-scale_removal
TOC concentration (mg L-1)
TOC removal (%)
TN concentration (mg L-1)
TN removal (%)
Time (d)
0
14
28
42
56
70
84
98
112
126
140

Figure 2

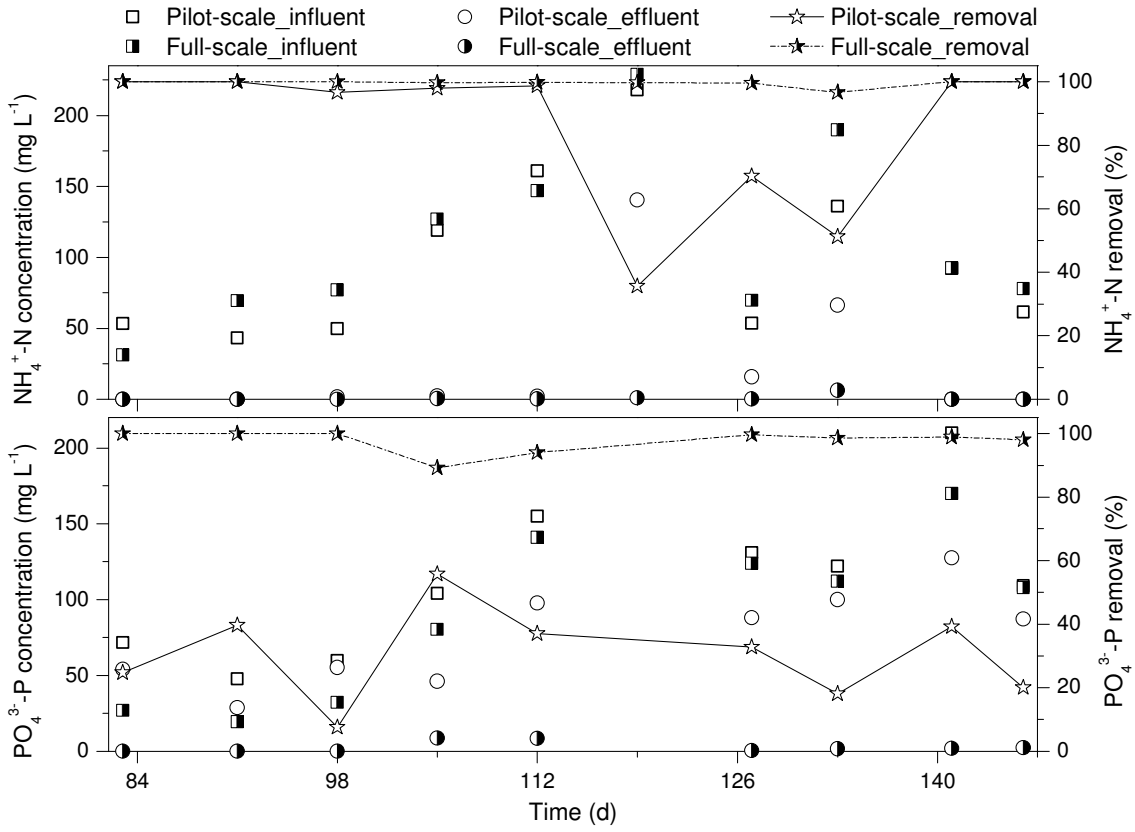
Pilot-scale_influent
Full-scale_influent
Pilot-scale_effluent
Full-scale_effluent
Pilot-scale_removal
Full-scale_removal
NH4+-N concentration (mg L-1)
NH4+-N removal (%)
PO43--P concentration (mg L-1)
PO43--P removal (%)
Time (d)
84
98
112
126
140

Figure 3

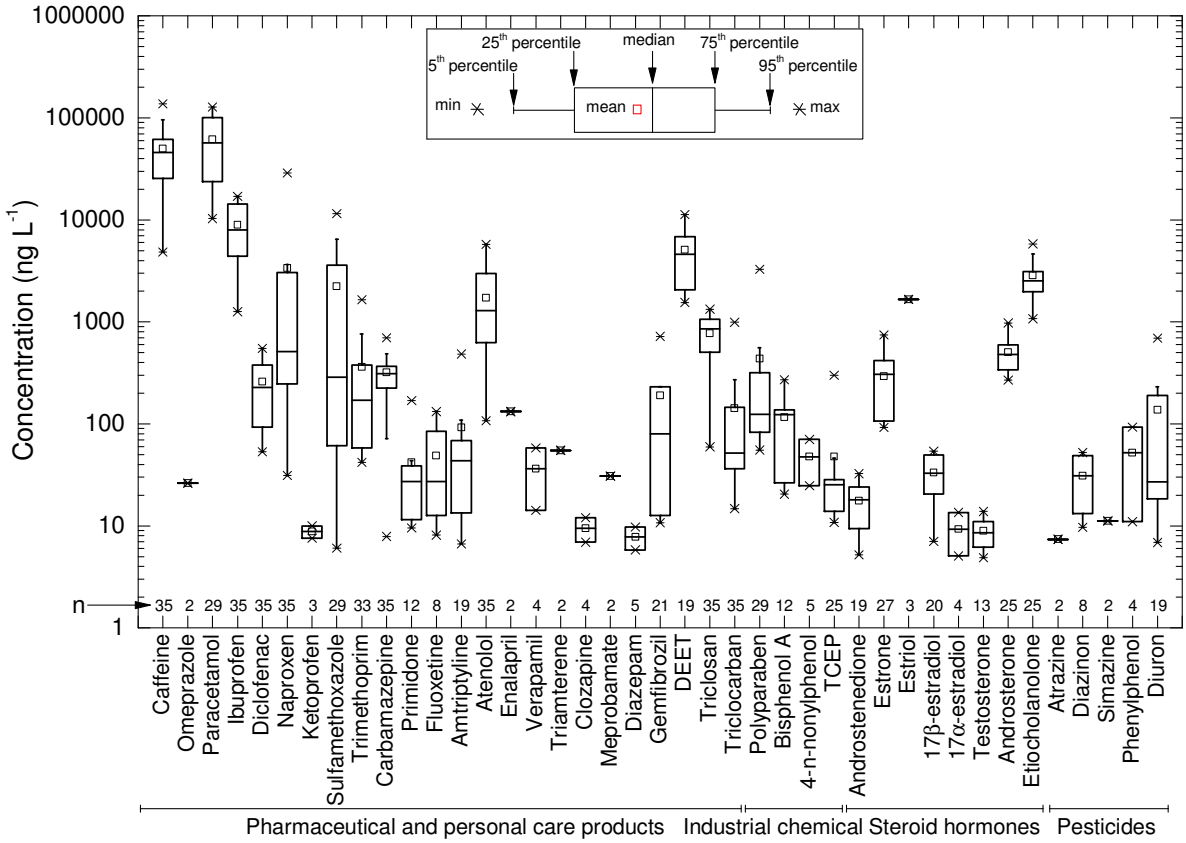
Concentration (ng L-1)
1000000
100000
10000
1000
100
10
1
n
25th percentile
median
75th percentile
5th percentile
95th percentile
min
mean
max
35 2 29 35 35 35 3 29 33 35 12 8 19 35 2 4 2 4 2 5 21 19 35 35 29 12 5 25 19 27 3 20 4 13 25 25 2 8 2 4 19
Caffeine
Omeprazole
Paracetamol
Ibuprofen
Diclofenac
Naproxen
Ketoprofen
Sulfamethoxazole
Trimethoprim
Carbamazepine
Primidone
Fluoxetine
Amtriptyline
Atenolol
Enalapril
Verapamil
Triamterene
Clozapine
Meprobamate
Diazepam
Gemfibrozil
DEET
Triclosan
Triclocarban
Polyparaben
Bisphenol A
4-n-nonylphenol
TCEP
Androstenedione
Estrone
Estriol
17β-estradiol
17α-estradiol
Testosterone
Androsterone
Etiocholanolone
Atrazine
Diazinon
Simazine
Phenylphenol
Diuron
Pharmaceutical and personal care products
Industrial chemical
Steroid hormones
Pesticides

Figure 4

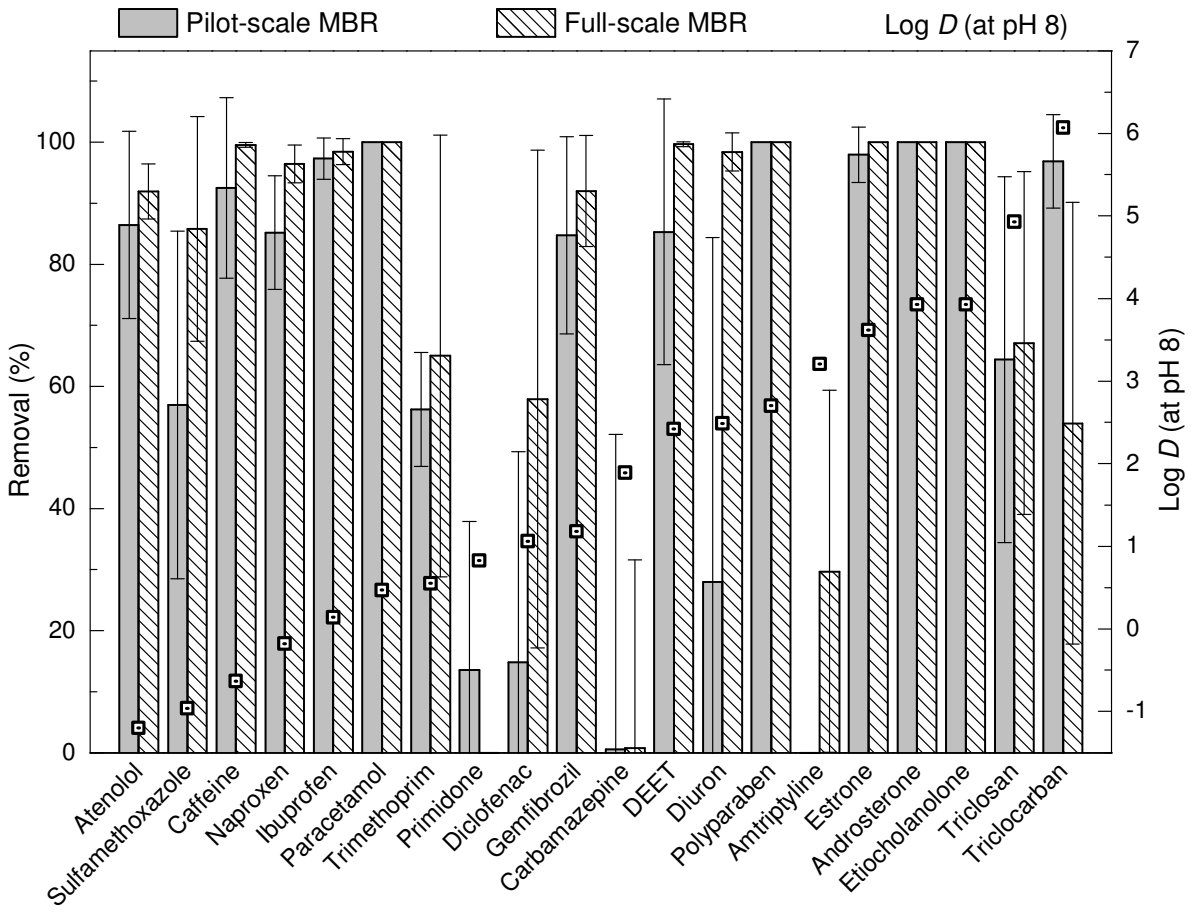
Pilot-scale MBR
Full-scale MBR
Log D (at pH 8)
Removal (%)
Log D (at pH 8)
0
20
40
60
80
100
-1
0
1
2
3
4
5
6
7
Atenolol
Sulfamethoxazole
Caffeine
Naproxen
Ibuprofen
Paracetamol
Trimethoprim
Primidone
Diclofenac
Gemfibrozil
Carbamazepine
DEET
Diuron
Polyparaben
Amtriptyline
Estrone
Androsterone
Etiocholanolone
Triclosan
Triclocarban

Figure 5

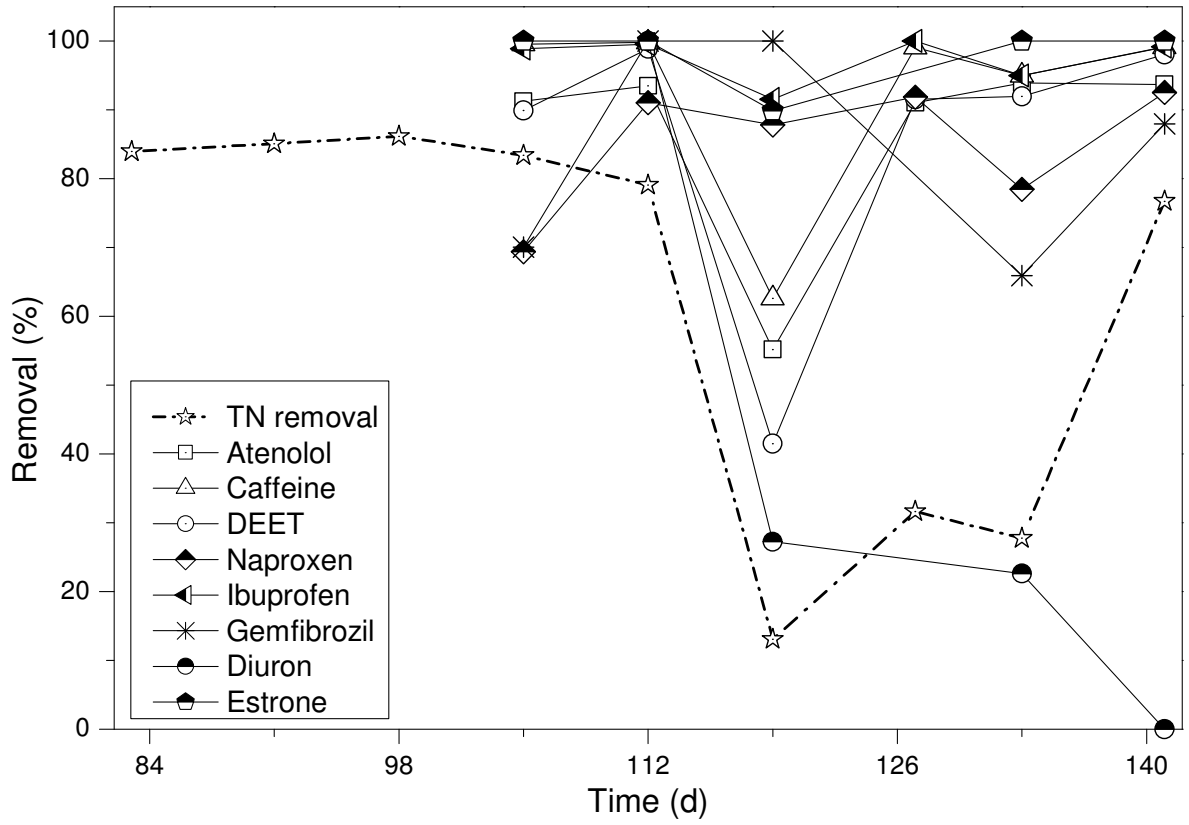
Removal (%)
Time (d)
TN removal
Atenolol
Caffeine
DEET
Naproxen
Ibuprofen
Gemfibrozil
Diuron
Estrone
0
20
40
60
80
100
84
98
112
126
140

Figure 6

SUPPLEMENTARY DATA

Nutrient and trace organic contaminant removal from wastewater of a resort town: comparison between a pilot and a full scale membrane bioreactor

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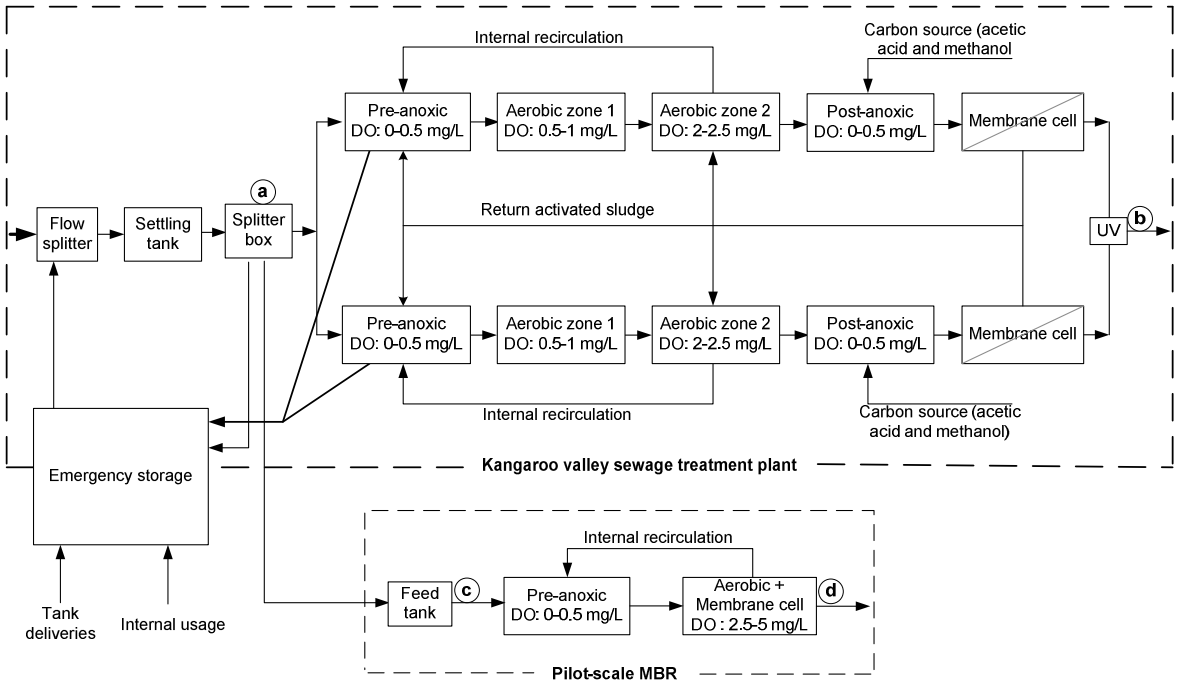

Figure S7: Layout of the full- and pilot-scale membrane bioreactors (MBRs), summarizing the key components. ‘a’ and ‘b’ indicate influent and effluent sampling points for the full-scale MBR. ‘c’ and ‘d’ indicate influent and effluent sampling points for the pilot MBR.

Table S2. Trace organic contaminant analysis

Table S2-a. Method description

Analytical methods using electrospray ionization (ESI) are based on that of Vanderford et al. Environmental Science and Technology, **2006**, volume 40, pp 7312-7320. The method employing atmospheric pressure chemical ionization (APCI) was based on that reported by Vanderford et al. Analytical Chemistry, **2003**, volume 75, pp 6265-6274.

Solid-Phase Extraction. Analytes were extracted using 5 mL, 500 mg hydrophilic/lipophilic balance (HLB) cartridges (Waters, Millford, MA, USA). Cartridges were pre-conditioned with 5 mL of methanol and 5 mL of reagent water. Samples were spiked with a solution containing 50 ng of an isotopically labeled version of each analyte. The sample was then loaded onto the cartridges at 10 mL min^{-1}, after which the cartridges were rinsed with 5 mL of reagent water and dried with a stream of nitrogen for 30 min. Loaded cartridges were stored at 4 °C in sealed bags under nitrogen until elution and analysis. Analytes were eluted from the cartridges with 5 mL of methanol followed by 5 mL of 1/9 (v/v) methanol/MTBE into centrifuge tubes. The resulting extract was concentrated using vacuum assisted evaporation to approximately 100 µL. The extract was brought to a final volume of 1mL with methanol.

Liquid Chromatography. Analytes were separated using an Agilent (Palo Alto, CA, USA) 1200 series high performance liquid chromatography (HPLC) system equipped with a 150 x 4.6 mm, 5 µm particle size, Luna C18 (*2*) column (Phenomenex, Torrence CA, USA) . A binary gradient consisting of 5 mM ammonium acetate in water (A) and 100% methanol (B) at a flow rate of 800 µL min^{-1} was used. For ESI positive analyses, the gradient was as follows: 10% B held for 0.50 min, stepped to 50% B at 0.51 min and increased linearly to 100% B at 8 min, then held at 100% B for 2 min. For ESI negative analyses, the gradient was as follows: 10% B held for 0.50 min, stepped to 60% B at 0.51 min and increased linearly to 100% B at 8 min, then held at 100% B for 3 min. A 5 min equilibration step at 10% B was used at the beginning of each run. For APCI analysis the eluants consisted of milli-Q grade water (A) and 0.1% v/v formic acid in methanol with the following ramp at a flow rate of 700 µL min^{-1}. 60% B held for 5 min, increased linearly to 100% B at 20 min, then held at 100% B for 3 min. A 3 min equilibrium step preceded injection. An injection volume of 10 µL was used for all methods.

Mass Spectrometry. Mass spectrometry was performed using an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) equipped with a turbo-V ion source employed in both positive and negative electro-spray modes. Steroids were analysed the source configured for (APCI) in positive mode. Using multiple reaction monitoring (MRM) two mass transitions for all but three of the analytes were monitored for unequivocal confirmation. One mass transition for the labeled internal standard was monitored. Only the first transition was used for quantitiation. Relative retention times of the analyte and isotopically labeled internal standard were also monitored to ensure correct identification.

Calibration and limits of Detection. Standard solutions of all analytes were prepared at 1, 5, 10, 50, 100, 500 and 1000 ng mL^{-1}. A relative response ratio of analyte/internal standard over a 1 – 1000 ng concentration range was generated enabling quantitation with correction for losses due to ion suppression and incomplete SPE recovery. All calibration curves had a correlation coefficient of 0.99 or better. Detection limits were defined as the concentration of an analyte giving a signal to noise (s/n) ratio greater than 3. The Limits of Reporting were determined using a s/n ratio of greater than 10.

Table S2-b. Transitions for compounds using ESI positive mode

Compound	Precursor Ion ($m\ z^{-1}$)	Product Ion ($m\ z^{-1}$)
Atenolol 1	267.2	145.1
Atenolol 2	267.2	190.2
Atenolol-D7	274.1	145.1
Paracetamol	152.1	110.1
Paracetamol-$^{15}N^{13}C$	155.0	111.0
Sulfamethoxazole 1	254.0	156.1
Sulfamethoxazole 2	254.0	92.0
Sulfamethoxazole-D4	258.1	160.1
Caffeine 1	195.0	138.1
Caffeine 2	195.0	110.1
Caffeine-D9	204.1	144.2
Trimethoprim 1	291.1	230.2
Trimethoprim 2	291.1	261.1
Trimethoprim-D9	300.3	234.2
TCEP 1	284.9	223.0
TCEP 2	284.9	62.9
Dilantin 1	253.1	182.1
Dilantin 2	253.1	104.1
Dilantin-D10	263.1	192.2
Carbamazepine 1	237.0	194.2
Carbamazepine 2	237.0	192.1
Carbamazepine-D10	247.1	204.3
Norfluoxetine 1	296.0	134.0
Norfluoxetine 2	296.0	30.2
Norfluoxetine-D5	301.0	139.0
Fluoxetine 1	310.0	44.1
Fluoxetine 2	310.0	148.2
Fluoxetine-D5	315.1	44.2
Enalapril 1	377.1	234.1
Enalapril 2	377.1	91.1
Enalapril-D5	382.2	239.2
Risperidone 1	411.1	191.2
Risperidone 2	411.3	110.0
Risperidone-D4	415.1	195.2
Atrazine 1	216.0	174.2
Atrazine 2	216.0	96.1
Atrazine-D5	221.3	179.1
Linuron 1	249.0	182.2
Linuron 2	249.0	160.1
Linuron-D6	255.0	160.1
Atorvastatin 1	559.1	440.1
Atorvastatin 2	559.1	250.3
Atorvastatin-D5	564.2	445.4
Omeprazole 1	346.2	198.2
Omeprazole 2	346.2	136.1
Omeprazole D3	349.2	198.0
Clozapine 1	327.1	270.2
Clozapine 2	327.1	192.1

Clozapine_D4	331.2	272.0
Amtriptyline 1	278.2	233.0
Amtriptyline 2	278.2	117.1
Amtriptyline-D6	284.4	233.1
DEET 1	192.2	119.0
DEET 2	192.2	108.9
DEET-D7	199.2	126.1
Primidone 1	219.2	162.2
Primidone 2	219.2	119.0
Primidone-D5	224.2	167.0
Verapamil 1	455.4	165.1
Verapamil 2	455.4	150.0
Verapamil-D6	461.4	165.2
Triamterene 1	254.2	237.0
Triamterene 2	254.2	104.0
Triamterene-D5	259.2	242.2
Polyparaben 1	181.2	139.1
Polyparaben 2	181.2	121.0
Metformin 1	130.1	113.1
Metformin 2	130.1	112.5
Metformin-D6	136.1	119.2
Meprobamate 1	218.9	158.2
Meprobamate 2	218.9	115.1
Meprobamate-D3	221.9	161.2
Hydroxyzine 1	375.3	201.1
Hydroxyzine 2	375.3	165.1
Hydroxyzine-D8	383.3	201.1
Diazepam 1	285.1	193.1
Diazepam 2	285.1	154.2
Diazepam-D5	290.1	198.1

Table S2-c. Transitions for compounds using ESI negative mode

Compound	Precursor Ion ($m\ z^{-1}$)	Product Ion ($m\ z^{-1}$)
Ketoprofen	252.8	208.8
Ketoprofen-D3	255.6	211.7
Naproxen 1	228.9	184.6
Naproxen 2	228.9	169.8
Naproxen-D3	231.9	187.8
Bisphenol A 1	226.9	211.8
Bisphenol A 2	226.9	132.9
Bisphenol A-D6	232.9	214.9
Ibuprofen 1	204.9	160.8
Ibuprofen 2	204.9	158.8
Ibuprofen-D3	208.0	163.9
Gemfibrozil 1	248.9	120.8
Gemfibrozil 2	248.9	126.8
Gemfibrozil-D6	254.9	120.9
Triclosan	286.6	35.0
Triclosan-D3	289.7	34.9
Simvastatin-hydroxyacid 1	435.1	318.9

Simvastatin-hydroxyacid 2	435.1	114.9
Simvastatin-hydroxyacid-D6	441.1	319.0
Simvastatin 1	399.0	114.9
Simvastatin 2	399.0	282.8
Simvastatin-D6	405.4	121.1
Diclofenac 1	293.9	249.7
Diclofenac 2	293.9	213.7
Diclofenac-D4	297.9	253.8
Triclocarban 1	312.9	159.8
Triclocarban 2	312.9	125.7
Triclocarban-D4	317.0	159.8
t-Octylphenol 1	205.2	132.9
t-Octylphenol 2	205.2	134.0
n-Octylphenol-D17	222.1	108.0
Polyparaben 1	179.0	135.7
Polyparaben 2	179.0	136.9
Phenylphenol 1	168.9	114.8
Phenylphenol 2	168.9	140.8
Nonylphenol 1	219.0	106.0
Nonylphenol 2	219.0	119.0
Nonylphenol-D4	223.1	110.0

Table S2-d. Transitions for compounds using APCI positive mode

Compound	Precursor Ion ($m\ z^{-1}$)	Product Ion ($m\ z^{-1}$)
Estriol 1	271.1	253.1
Estriol 2	271.1	133.0
Estriol-D2	273.2	255.2
Androstendione 1	287.2	97.1
Androstendione 2	287.2	109.2
Androstendione-D3	290.2	100.1
Etiocholanolone 1	273.2	255.3
Etiocholanolone 2	273.2	91.1
Etiocholanolone-D2	275.2	257.1
Androsterone 1	273.2	255.2
Androsterone 2	273.2	91.0
Estrone 1	271.2	159.2
Estrone 2	271.2	133.0
Estrone-D4	275.1	161.0
17β-Estradiol 1	255.2	159.3
17β-Estradiol 2	255.2	133.2
17β-Estradiol-D4	259.1	161.1
17α-Estradiol 1	255.2	159.3
17α-Estradiol 2	255.2	133.2
17α-Ethynylestradiol 1	279.2	133.1
17α-Ethynylestradiol 2	279.2	159.2
17α-Ethynylestradiol-D4	283.1	135.1
Testosterone 1	289.2	97.2
Testosterone 2	289.2	109.1
Testosterone-D2	291.2	99.1

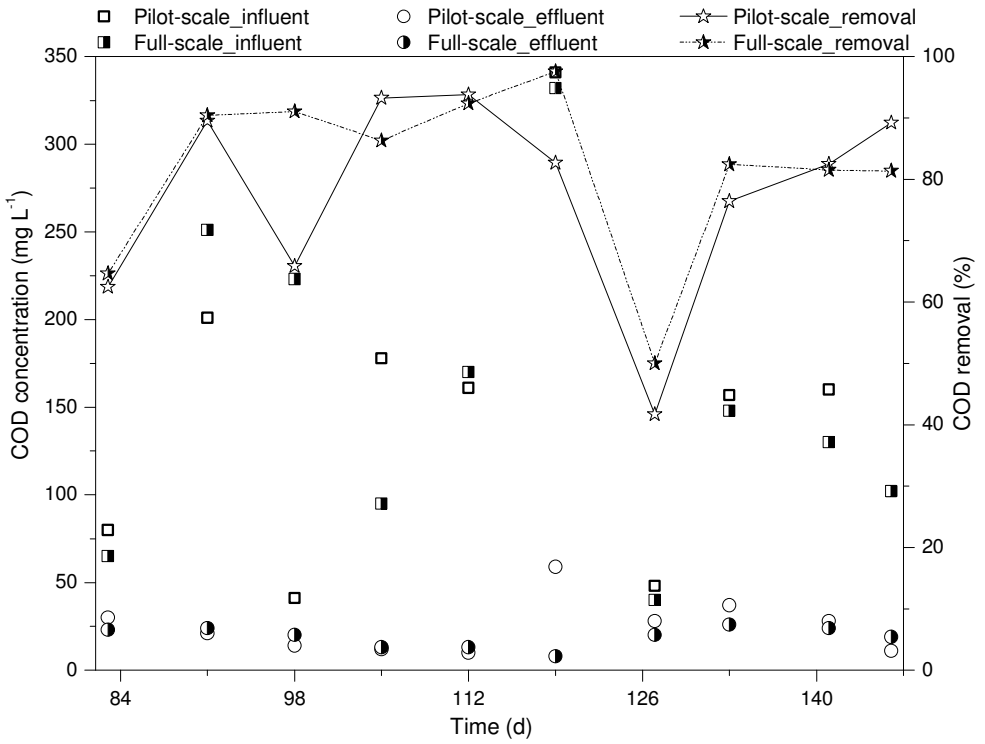

Figure S3: Chemical oxygen demand (COD) concentration and removal by the pilot- and full- scale MBRs (Pilot MBR operation scheme: Day 1-76, acclimatization; Day 77-146, period of pilot-and full-scale performance comparison).

Table S4: Raw sewage concentration (ng L^{-1}) of 45 monitored trace organic contaminants (TrOCs) including 27 pharmaceutical and personal care products (PPCPs), four industrial xenoestrogens, eight steroid hormones and six pesticides. In total, 35 samples were collected from 15 sampling events in duplicate (the first ten sampling events) or triplicate (the last five sampling events) from November 2012 to October 2014.

Compounds	Detection limit	13 November 2012		27 June 2013		29 July 2013		22 April 2014		29 April 2014		6 May 2014	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
Phamarceutical and personal care products (PPCPs)													
Caffeine	10	52000	49000	3810	5840	43000	49800	29200	30200	41800	40800	137400	138200
Omeprazole	5	26	26	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Paracetamol	5	<5	<5	8660	13400	55700	55800	53800	61200	24400	N.Q.	N.Q.	N.Q.
Ibuprofen	5	16520	17560	1040	1470	4530	4260	7300	6440	7800	7880	15520	16620
Diclofenac	5	556	546	43	64	86	88	106	114	476	624	356	380
Naproxen	5	27000	30600	23	39	224	226	1296	1286	440	484	8000	9660
Ketoprofen	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Sulfamethoxazole	5	<5	<5	<5	<5	7	6	161	177	<5	21	<5	<5
Trimethoprim	5	40	56	<5	<5	57	59	41	43	764	1118	114	468
Carbamazepine	5	660	740	6	10	73	71	230	222	302	306	356	374
Primidone	5	<5	<5	<5	<5	<5	<5	11	12	<5	<5	21	23
Fluoxetine	5	118	146	<5	<5	<5	<5	46	28	8	9	<5	<5
Amtriptyline	5	290	676	9	15	7	<5	48	38	52	54	41	47
Atenolol	5	5400	6140	79	136	196	191	648	598	900	880	4040	3180
Enalapril	5	129	135	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Verapamil	5	52	65	<5	<5	<5	<5	19	9	<5	<5	<5	<5
Triamterene	5	52	58	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Clozapine	5	<5	<5	5	9	<5	<5	15	9	<5	<5	<5	<5
Meprobamate	5	<5	<5	<5	<5	<5	<5	32	29	<5	<5	<5	<5
Diazepam	5	5	7	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Gemfibrozil	5	42	40	474	974	613	606	67	61	96	97	<5	11

DEET	5	10380	12180	Not measured				2040	1978	4660	4560	7140	6640
Triclosan	5	866	900	52	67	149	178	1308	1298	1304	1358	1020	1120
Triclocarban	10	880	1110	12	18	17	18	164	127	138	102	24	19
Dilantin	5	Not measured						<5	<5	<5	<5	<5	<5
Risperidone	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Hydroxyzine	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Industrial chemicals													
Polyparaben	10	3500	3080	89	44	457	461	148	97	78	77	180	174
TCEP	10	304	296	<10	<10	<10	<10	57	35	26	28	24	27
Bisphenol A	20	20	21	27	<20	129	147	143	396	N.Q.	N.Q.	N.Q.	N.Q.
4-n-nonylphenol	5	<5	<5	<5	<5	<5	<5	93	48	<5	<5	<5	<5
Steroid hormones													
Androstendione	5	Not measured						<5	<5	11	11	5	6
Estrone	5	Not measured						298	326	458	432	834	656
Estriol	5	Not measured						NQ	NQ	NQ	NQ	NQ	NQ
17β-estradiol	5	Not measured						16	15	24	28	40	39
17α-estradiol	5	Not measured						<5	5	<5	14	<5	<5
Testosterone	5	Not measured						<5	<5	6	7	8	9
Androsterone	5	Not measured						286	260	316	362	556	566
Etiocholanolone	5	Not measured						1578	1624	1928	2040	3100	3140
Pesticides													
Atrazine	5	<5	<5	<5	<5	6	9	<5	<5	<5	<5	<5	<5
Diazinon	10 (5)*	53	52	<10	<10	<10	<10	<5	<5	<5	10	<5	<5
Simazine	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Phenylphenol	10 (20)*	94	92	<10	<10	<10	11	<20	<20	<20	<20	<20	<20
Diuron	5 (10)*	178	202	23	38	7	7	<10	<10	16	20	29	25
Linuron	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5

Table S4 (continued)

Compounds	Detection limit	14 May 2014		20 May 2014		28 May 2014		2 June 2014		30 June 2014		
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 3
Phamarceutical and personal care products (PPCPs)												
Caffeine	10	13440	12840	26000	25400	32000	30400	13680	12480	57600	64600	60000
Omeprazole	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Paracetamol	5	<5	<5	23000	23600	28800	22200	10660	10040	123200	110400	124600
Ibuprofen	5	1736	1738	7840	8160	3440	3140	4780	4980	14600	13900	14460
Diclofenac	5	258	270	131	134	95	92	224	232	228	224	222
Naproxen	5	3040	3080	1468	1506	494	448	508	516	248	242	246
Ketoprofen	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Sulfamethoxazole	5	87	77	2340	2360	378	344	6680	6200	5140	4640	4820
Trimethoprim	5	108	94	79	86	55	61	396	362	734	778	780
Carbamazepine	5	476	500	306	314	346	322	338	348	232	228	226
Primidone	5	163	176	32	36	47	40	33	32	<5	<5	<5
Fluoxetine	5	18	16	<5	<5	<5	<5	<5	<5	<5	<5	<5
Amtriptyline	5	114	105	17	10	<5	<5	<5	<5	70	66	70
Atenolol	5	1302	1388	652	690	548	594	740	740	2080	2080	1984
Enalapril	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Verapamil	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Triamterene	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Clozapine	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Meprobamate	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Diazepam	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Gemfibrozil	5	<5	<5	226	234	113	110	12	13	<5	<5	<5

DEET	5	10240	10740	1784	2340	4620	4660	2080	2080	1540	1566	1540
Triclosan	5	624	384	900	810	712	680	616	400	640	596	748
Triclocarban	10	46	43	39	45	40	38	50	54	148	167	155
Dilantin	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Risperidone	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Hydroxyzine	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Industrial chemicals												
Polyparaben	10	<10	<10	<10	<10	<10	<10	52	59	600	542	536
TCEP	10	13	15	<10	19	28	28	27	28	<10	<10	<10
Bisphenol A	20	NQ	NQ	NQ	NQ	107	118	109	157	NQ	NQ	NQ
4-n-nonylphenol	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	25	<5
Steroid hormones												
Androstendione	5	<5	<5	33	32	8	8	23	25	19	18	18
Estrone	5	<5	<5	162	167	93	96	95	90	206	200	197
Estriol	5	<5	<5	NQ	NQ	NQ	NQ	NQ	NQ	1066	3520	394
17β-estradiol	5	<5	<5	<5	<5	<5	<5	<5	7	55	47	56
17α-estradiol	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Testosterone	5	<5	<5	<5	<5	<5	<5	<5	<5	15	13	14
Androsterone	5	<5	<5	676	520	450	424	<5	<5	264	266	274
Etiocholanolone	5	<5	<5	6320	5360	4600	4680	<5	<5	1068	1056	1094
Pesticides												
Atrazine	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Diazinon	5	<5	<5	<5	<5	<5	<5	<5	<5	17	17	17
Simazine	5	11	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Phenylphenol	20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Diuron	5	<10	<10	230	232	19	18	26	26	712	680	680
Linuron	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5

Table S4 (continued)

Compounds	Detection limit	26 August 2014			5 September 2014			22 September 2014			2 October 2014		
		Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Phamarceutical and personal care products (PPCPs)													
Caffeine	10	91800	98600	97800	64200	60200	59400	82800	93200	99800	49800	43800	43400
Omeprazole	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Paracetamol	5	83000	67800	84200	111200	108800	128800	111600	80800	65400	103200	118200	162400
Ibuprofen	5	9820	10480	9920	9680	8560	8360	12440	12520	12000	17820	15760	17000
Diclofenac	5	366	382	386	60	53	52	492	484	464	334	338	318
Naproxen	5	1176	1196	1158	41	33	32	330	296	328	3660	3800	3520
Ketoprofen	5	<5	11	4	<5	<5	<5	<5	<5	10	<5	<5	<5
Sulfamethoxazole	5	185	234	220	12340	10620	11540	826	814	908	39	48	33
Trimethoprim	5	61	63	108	1830	1532	1580	336	286	340	246	230	244
Carbamazepine	5	564	624	618	376	348	332	312	288	290	158	150	162
Primidone	5	<5	<5	<5	<5	<5	<5	10	<5	<5	<5	12	<5
Fluoxetine	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Amtriptyline	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Atenolol	5	2740	3040	3180	1418	1240	1210	3480	3200	3400	1600	1540	1656
Enalapril	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Verapamil	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Triamterene	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Clozapine	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Meprobamate	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5

Diazepam	5	10	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Gemfibrozil	5	10	11	12	<5	<5	<5	<5	<5	<5	<5	<5	<5
DEET	5	Not measured											
Triclosan	5	404	452	512	1178	1188	1076	1154	874	1110	968	960	910
Triclocarban	10	42	75	72	103	100	110	218	284	308	51	27	32
Dilantin	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Risperidone	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Hydroxyzine	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Industrial chemicals													
Polyparaben	10	127	123	130	96	84	83	116	98	113	134	128	112
TCEP	10	16	14	13	<10	<10	<10	14	11	12	11	11	<10
Bisphenol A	20	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
4-n-nonylphenol	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Steroid hormones													
Androstendione	5	<5	<5	<5	19	17	17	30	21	22	<5	<5	<5
Estrone	5	364	258	300	103	112	105	306	332	376	402	428	430
Estriol	5	NQ	NQ	NQ	NQ	NQ	<10	NQ	NQ	NQ	NQ	NQ	NQ
17β-estradiol	5	48	45	47	<5	<5	<5	29	21	29	54	57	51
17α-estradiol	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Testosterone	5	<5	<5	<5	6	5	4	12	11	10	<5	<5	<5
Androsterone	5	490	426	442	1044	1028	864	622	638	590	532	500	482
Etiocholanolone	5	2480	2140	2220	3340	3120	2700	2800	2740	2780	2340	2140	2200
Pesticides													
Atrazine	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Diazinon	5	<5	<5	<5	<5	<5	<5	47	43	45	<5	<5	<5
Simazine	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Phenylphenol	20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20

Diuron	5	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Linuron	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5

*The detection limit of diazinon, phenylphenol and diuron were 10, 10, and 5 ng L^{-1}, respectively for first six samples collected in 2012 and 2013, but then changed to 5, 20, and 10 ng L^{-1}, respectively, for the rest of the samples

NQ: not quantifiable.

Table S5: Concentration (ng $_{TrOC}$ g^{-1} $_{MLSS}$) of TrOCs in sludge (BDL = Below detection limit; NQ= Not quantifiable).

Compounds	Sample 1	Sample 2
Atenolol	BDL	36
Sulfamethoxazole	BDL	11
Caffeine	BDL	BDL
Naproxen	BDL	BDL
Ibuprofen	BDL	BDL
Paracetamol	17	BDL
Trimethoprim	42	45
Primidone	BDL	BDL
Diclofenac	13	12
Gemfibrozil	BDL	BDL
Carbamazepine	9	9
DEET	NQ	NQ
Diuron	BDL	BDL
Polyparaben	BDL	BDL
Amtriptyline	BDL	BDL
Estrone	BDL	BDL
Androsterone	NQ	NQ
Etiocholanolone	NQ	NQ
Triclosan	230	191
Triclocarban	786	1128

Note:

1. TrOC concentration in sludge was not measured during the period of aqueous phase TrOC removal comparison between pilot- and full-scale MBRs (Day 105- 146). The pilot-scale MBR was continued to be operated beyond that, and TrOC concentration in sludge was measured on Day 174 when the TOC, TN and TrOC concentrations were at levels similar to that during Day 105 – 146.

2. Regarding 'BDL': TrOCs from 0.5 g sludge (dry weight) was extracted (see Materials and Methods) into liquid samples on which TrOC analysis was conducted. Liquid samples which returned concentrations below the detection limits (see Table S3) has been marked with 'BDL' here.

Table S6: Statistical analysis of pilot- vs full-scale MBR TrOC removal data depicted in Figure 4 of the main manuscript (paired *t*-test was conducted using Microsoft Excel. Values of $p < 0.05$ were considered to indicate statistical significance)

Compounds	*p* value
Atenolol	0.210
Sulfamethoxazole	0.047
Caffeine	0.134
Naproxen	0.009
Ibuprofen	0.257
Paracetamol	-
Trimethoprim	0.289
Primidone	0.174
Diclofenac	0.038
Gemfibrozil	0.206
Carbamazepine	0.455
DEET	0.068
Diuron	0.023
Polyparaben	-
Amtriptyline	0.020
Estrone	0.173
Androsterone	-
Etiocholanolone	-
Triclosan	0.437
Triclocarban	0.009

Table S7: Comparison of influent TrOC concentrations (ng L^{-1}) – all available samples (see Table S4) vs samples used for performance comparison between pilot-scale and full-scale MBRs (n = number of samples).

TrOC	Detection limit	All available samples				Samples during period of comparison: pilot-scale vs full-scale MBR			
		n	Max	Min	Median	n	Max	Min	Median
Atenolol	5	35	6140	79	1388	12	4040	548	785
Sulfamethoxazole	5	35	12340	5	185	12	2360	5	124
Caffeine	10	35	138200	3810	49000	12	138200	12840	30300
Naproxen	5	35	30600	23	508	12	9660	440	1382
Ibuprofen	5	35	17820	1040	8560	12	16620	1736	7550
Paracetamol	5	32	162400	5	58500	9	61200	5	23600
Trimethoprim	5	35	1830	5	114	12	1118	41	90
Primidone	5	35	176	5	5	12	176	5	27
Diclofenac	5	35	624	43	232	12	624	92	196
Gemfibrozil	5	35	974	5	11	12	234	5	81
Carbamazepine	5	35	740	6	312	12	500	222	318
DEET	5	19	12180	1540	4560	12	10740	1784	4640
Diuron	10	35	712	7	10	12	232	10	18
Polyparaben	10	35	3500	10	112	12	180	10	44
Amtriptyline	5	35	676	5	7	12	114	5	44
Estrone	5	29	834	5	258	12	834	5	233
Androsterone	5	29	1044	5	450	12	676	5	393
Etiocholanolone	5	29	6320	5	2220	12	6320	5	2570
Triclosan	5	35	1358	52	866	12	1358	384	960
Triclocarban	10	35	1110	12	54	12	164	19	44

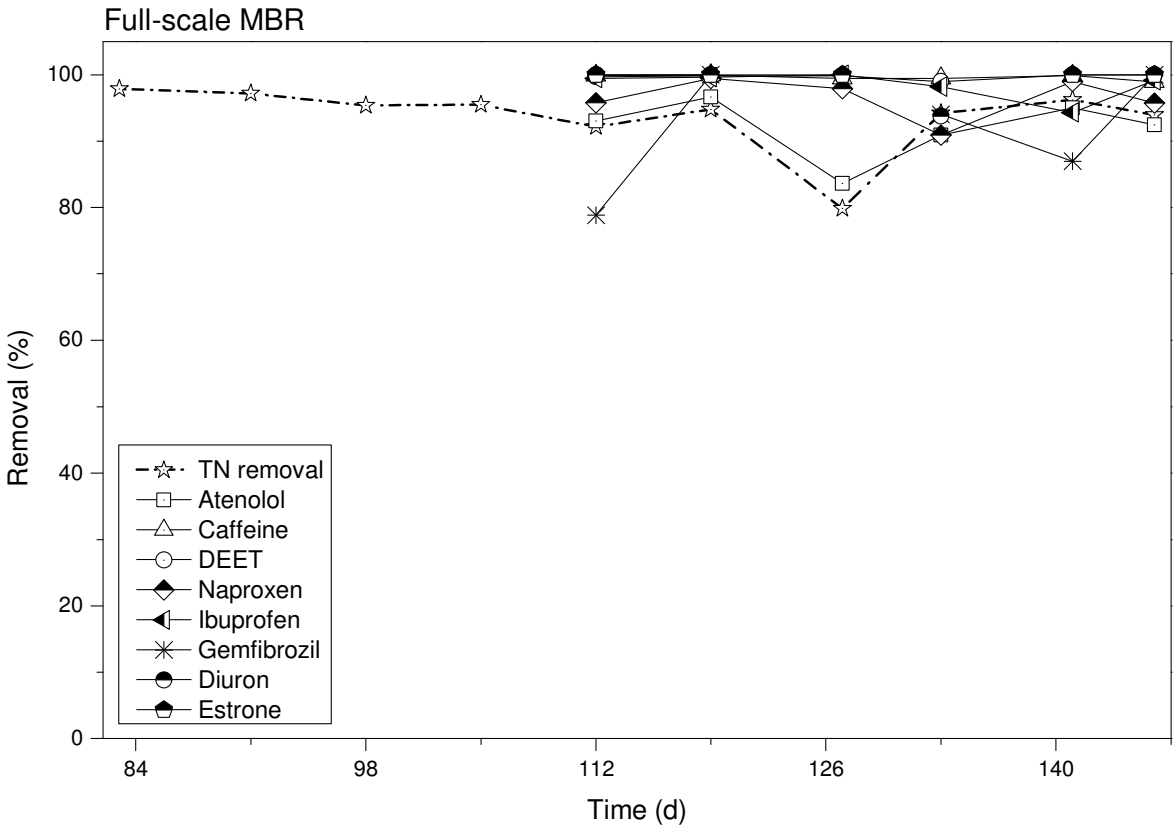

Figure S8: Variation in TN and TrOC removal by the full-scale MBR (TOC and TN removal by the full- and pilot-scale MBR was compared from Day 77 to 146; however TrOC removal was monitored from Day 105 to 146).